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54 Ink jet recording sheet.

57 An ink jet recording sheet comprising a paper support applied on at least one surface thereof or internally with a composition which comprises an aqueous dispersion of polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer or a mixture thereof serving as a binder or sizing agent and a white filler. The white filler is contained in a weight ratio, to the binder, of 10:1 to 0.2:1 when the composition is applied on the surface of the paper support. When the composition is internally incorporated in the recording sheet, it comprises 10 to 60 parts by weight of the filler and 2 to 20 parts by weight of the binder per 100 parts by weight of pulp.

EP 0 046 416 A2

- 1 -

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DESCRIPTION

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INK JET RECORDING SHEET

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This invention relates to ink jet recording and more particularly, to recording papers for the ink jet recording.

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Great interest has recently been attracted to the recording by ink jet systems because of their reduced noises, ease in color recording, possibility of high speed recording, and utilization of ordinary papers. The ink jet systems are now being used widely in the field of facsimile, various types of printers and the like. It is generally accepted that ordinary papers are satisfactorily usable as recording paper for use in the ink jet recording system. However, this does not mean that all the ordinary papers which are widely used at present are usable. In order to obtain recorded matters of more excellent quality, the recording paper itself should meet several requirements which follow: (1) The paper has an excellent ink receptivity to allow ink dots deposited on the paper surface to be rapidly absorbed in the inside of paper; and (2) The paper can suppress ink dots applied on the surface from running or spreading.

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The requirement (1) is the most fundamental one which must be furnished with ink jet recording papers and

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1 assumes great importance especially when color images are
2 produced by the ink jet system. This is because in order
3 to produce color images, it is necessary to make a variety
4 of colors from combinations of yellow, cyan and magenta
5 inks, so that inks of different colors are deposited on the
6 same portion of paper surface, resulting in large amounts
7 of inks per unit area.

8 The requirement (2) is necessary for
9 obtaining clear recorded matters. By preventing ink dots
10 from spreading, the optical density of recorded matter can
11 be increased. In general, the simplest method of
12 increasing the optical density of recorded matter is to
13 increase the concentration of dye in ink. However, this
14 method has its limit because of the tendency to clog a head
15 nozzle. Accordingly, it is important that recording papers
16 satisfy the above requirement.

17 Aside from the fundamental requirements (1) and (2),
18 recording papers should satisfy the following further
19 requirements: (3) The degree of penetration of ink in the
20 direction of depth or in the longitudinal direction is not
21 too great; and (4) The paper has an excellent brightness.
22 The optical density of recorded matter largely depends on
23 the state of the paper surface and if the degree of the
24 penetration in the direction of depth is too great, it is
25 difficult to make the optical density high.

- 2 -

1 The recording paper to be applied in the ink jet
2 recording system is generally made from bleached chemical
3 pulp to which fillers, dyes and, if required, sizing agents
4 and strength improvers are added.

5 There have heretofore been proposed several types of
6 papers for ink jet recording. For instance, Japanese
7 Laid-open Patent Application No. 52-74340 discloses an ink
8 jet recording paper which is characterized in that a ratio
9 of an air resistance to basis weight (g/m^2) (air resist-
10 ance/basis weight) is below 0.3 and that when an aqueous
11 ink for ink jet recording is dropped in an amount of 0.004
12 ml, an absorption time of ink is in the range of from two
13 seconds to 60 seconds. Further, Japanese Laid-open Patent
14 Application No. 52-53012 teaches a method of making
15 recording papers which is characterized by applying a
16 coating to a base paper which has been incorporated with a
17 wet strength improver known per se and which has a Stockigt
18 sizing degree of below 1 second whereby the resulting
19 surface coated paper has a Stockigt sizing degree of below
20 3 seconds. In these laid-open patent applications, there
21 are described surface sizing agents including oxidized
22 starch, PVA, galactomannon gum, polyacrylamide, sodium
23 alginate, styrene-maleic acid copolymer, CMC and other
24 cellulose derivatives, casein, soy bean protein and the
25 like. In addition, there are

1 mentioned, as sizing additives, hydrophobic materials or
2 latices, rosin and its derivatives, petroleum resins,
3 fumaric acid, maleic acid its derivatives, waxes, synthetic
4 resins, fatty acids, alkylketene dimers and the like, and,
5 as pigment or filler, kaolin, calcium carbonate, aluminium
6 hydroxide, satin white, titanium oxide, and urea-formalin
7 organic fillers.

8 Moreover, there is proposed in Japanese Laid-open
9 Patent Application No. 55-5830 a sheet for ink jet
10 recording which comprises a support and an ink-receptive
11 layer formed on the surface of the support, said sheet
12 having an opacity of 55.0 to 97.5%, an absorptivity of the
13 ink-receptive layer being in the range of 1.5 to 18.0
14 mm/min. Also, Japanese Laid-open Patent Application No.
15 55-11829 teaches a sheet for ink jet recording which has
16 (1) two or more layers, (2) an opacity of 55.0 to 97.5%,
17 (3) a top layer with a thickness of 1.0 to 16.0 microns,
18 and (4) an ink-receptivity of the top layer of 1.5 to 5.5
19 mm/min and that of a second layer of 5.5 to 60.0 mm/min.
20 The ink-receptive layer of these sheets is formed of
21 white pigments such as clay, talc, diatomaceous earth,
22 calcium carbonate, calcium sulfate, barium sulfate,
23 titanium oxide, zinc oxide, zinc sulfide, satin white,
24 aluminium silicate, lithopone and the like. As binder
25 resin, there are mentioned oxidized starch, etherified

- 5 -

1 starch, gelatin, casein, carboxymethyl cellulose,
2 hydroethyethyl cellulose, polyvinyl alcohol and SBR latex.

3 We have made an extensive studies of ink jet
4 recording papers which satisfy the afore-mentioned
5 requirements (1) to (4) and found that coating layers made
6 of combinations of sizing agents or binder resins and
7 pigments and fillers which have been known from the prior
8 laie-open patent applications do not show satisfactory
9 characteristics when applied for such recording purpose.
10 Especislly, the resins serving as the sizing agent or
11 binder play an important role and it has been found that
12 the known resins are unsatisfactory in ink receptivity and
13 thus recorded matter using such resins as a surface coating
14 frequently shows insufficient optical density.

15 It is accordingly an object of the present invention
16 to provide an jet recording sheet which shows an improved
17 optical density, when recorded, over prior art
18 counterparts.

19 It is another object of the invention to provide an
20 ink jet recording sheet which shows an excellent ink
21 receptivity and is able to suppress ink dots from
22 spreading.

23 It is a further object of the invention to provide
24 an ink jet recording sheet which ensures a certain extent

- 5 -

1 of water proof and excellent fastness of light of recorded
2 matter.

3 According to the present invention, there is
4 provided a recording sheet for ink jet recording which
5 comprises a paper support applied on at least one surface
6 thereof or internally with a composition characterized in
7 that said composition comprises polyvinylpyrrolidone,
8 vinylpyrrolidone-vinyl acetate copolymer or a mixture
9 thereof serving as a binder or sizing agent and a white
10 filler, a said white filler being used in a weight ratio to
11 said binder of 10 : 1 to 0.2 : 1 when said composition is
12 applied on the surface of said paper support and said
13 composition comprising 10 to 60 parts by weight of said
14 white filler and 2 to 20 parts by weight of said binder per
15 100 parts by weight of stock pulp when said composition is
16 applied internally of the recording sheet.

1 As having described hereinabove, one of features of
2 the present invention resides in use of polyvinyl-
3 pyrrolidone (hereinafter abbreviated as PVP) and/or vinyl-
4 pyrrolidone-vinyl acetate copolymer (hereinafter
5 abbreviated as PVP/VAc). The PVP and PVP/VAc are
6 water-soluble polymers and have a film-forming property.
7 They are industrially applied as cosmetics, medical
8 supplies, adhesives, cleaning agents and soaps,
9 fiber-finishing agents, and inks, and also in the field of
10 lithographic printing and paper. PVP and PVP/VAc which are
11 applied in the field of the paper-making industry are used
12 as a decoloring agent for rags for regeneration, an
13 improver of cellulose paper to improve its tensile
14 strength, and a binder for the specific type of paper made
15 of inorganic flakes or fibers.

16 When applied to inks making use of dyes, PVP renders
17 the dye more readily soluble, serves to prevent gelation,
18 and imparts deep color tone to even inks of low concentration
19 of dye.

20 The PVP and PVP/VAc is soluble in water and
21 have generally an average molecular weight of several
22 thousands to several hundred thousands. These polymers may
23 be ones which are prepared by any of know techniques.

1 The commercially available vinylpyrrolidone and
2 vinyl acetate copolymer has a ratio of PV/VAc generally in
3 the range of 70/30 to 30/70.

4 The PVP and/or PVA/VAc is used in the practice of
5 the invention together with a white pigment or filler.
6 Examples of the filler which is preferably used in combi-
7 nation with the PVP resin or PVP/VAc copolymer as will
8 become apparent from examples appearing hereinafter include
9 clay, talc, calcium carbonate, calcium sulfate, calcium
10 silicate diatomaceous earth, magnesium silicate, terra alba,
11 activated clay, magnesium oxide, magnesium carbonate and
12 aluminium hydroxide. Aside from these, fillers which are
13 ordinarily employed in the paper-making industry such as
14 titanium oxide, silica, aluminium silicate, satin white,
15 zinc oxide and the like may be usable though they are
16 inferior in optical density and the other characteristics
17 to those mentioned above.

18 In one aspect of the invention, an aqueous dispersion
19 of the PVP and/or PVP/VAc and the filler is applied onto
20 at least one surface of paper support. The dispersion can
21 be readily prepared by adding a filler of a powder form
22 to an aqueous solution of the PVP and/or PVP/VAc. In this
23 case, a ratio of the filler to the resin is generally in
24 the range of 10 : 1 to 0.2 : 1, preferably 1 : 1 to 1 : 2.
25 This will be particularly described in examples appearing
26 hereinafter. The aqueous dispersion is applied to a paper

1 support, which may be any of papers ordinarily employed
2 for ink jet recording purpose, in an amount of 3 to 50 g/m²
3 on the dry basis. Preferably, the coating amount is in
4 the range of from 10 to 30 g/m² and most preferably about
5 20 g/m².

6 In order to improve water proof, the PVP and/or
7 PVP/VAc resin may be admixed with a sizing agent or binder
8 which is ordinarily employed in the paper-making industry,
9 including, for example, oxidized starch, PVA,
10 styrene-maleic acid copolymer, CMC, and
11 hydroxyethylcellulose. When the mixture is used, the PVP
12 and/or PVP/VAc resin should be contained in an amount of
13 not smaller than 33 wt% of the mixture when an added sizing
14 agent shows little or no water absorptivity and in an
15 amount of not smaller than 20 wt% of the mixture when an
16 added sizing agent shows water absorptivity such as PVA.

17 When it is desired to control a hardness of the
18 PVP/VAc film, there may be added to the aqueous dispersion
19 or composition as usual plasticizers such as dimethyl
20 phthalate, glycerine, diethylene glycol, sorbitol
21 allylsulfonamide-formaldehyde, cellulose butyrate, cellulose
22 butyrate-propionate and the like.

23 In another aspect of the present invention, the
24 aqueous dispersion or composition is mixed with stock pulp
25 and then an ink jet recording paper is made from the
26 mixture by any of known paper-making techniques. The paper

1 incorporating therein the PVP and/or PVP/VAc resin and
2 filler composition has several advantages: The making
3 process is simple; and The PVP or PVP/VAc is readily
4 soluble in water and is thus poor in water proof, so that
5 when a PVP or PVP/VAc-coated paper is dipped in water, the
6 coating layer is readily dissolved out but the internally
7 incorporated paper has a certain degree of water proof
8 though the filler is surely come off from the paper when
9 dipped in water. This is experimentally confirmed that
10 when a surface coated recording paper is vertically dipped
11 in water, a coating layer composed of PVP or PVP/VAc and
12 white filler is come off from the paper support in 5 to 10
13 seconds. On the other hand, even when the internally
14 incorporated recording paper is dipped in water for 10
15 seconds, only several percent of filler is found to be come
16 off from the paper. In addition, it takes over one minute
17 before the pulp stock of the paper itself is reduced into
18 pieces and dispersed in water. As a matter of course, such
19 a time varies depending on the amount of PVP or PVP/VAc. A
20 reason why the water proof is improved by internally
21 applying the composition is believed due to the fact that
22 the resin or binder component is uniformly mixed with a
23 pulp component and thus the speed of infiltration of water
24 becomes slow and no coating layer is come off as will be
25 experienced in the case of the surface coating.

26 The internally applied recording paper can be made
27 by one step without involving an additional coating process
28 and is thus much simpler in manufacturing step than the

1 surface-coated recording paper.

2 However, the resin and filler are usually in the
3 case in amounts greater than those required for the surface
4 coating technique. That is, as having defined
5 hereinbefore, the PVP and/or PVP/VAc is used in an amount
6 of 2 to 20 parts by weight and a white filler is used in an
7 amount of 10 to 60 parts by weight both per 100 parts by
8 weight of stock pulp. The amount of the white filler, of
9 course, varies more or less depending on the type of the
10 filler.

11 In order to further and much improve the water proof
12 of either type of the recording papers, it is favorable to
13 add to the PVP or PVP/VAc resin binder an aqueous emulsion-type
14 resin or a polymer soluble in alcohol which is capable
15 of forming a water-proof film after drying. Water-soluble
16 resin binders such as oxidized starch, PVA, CMC,
17 hydroxyethyl cellulose and the like serve to improve the
18 water proof as having described hereinbefore when used in combination
19 with PVP or PVP/VAc but are not potential for such purpose. For
20 instance, the coating layer obtained from the mixture of
21 the water-soluble resin binder and PVP or PVP/VAc is
22 dissolved in water in about 10 to 15 seconds and an
23 increasing amount of the water-soluble resin binder gives
24 an adverse influence of ink receptivity.

25 Examples of the aqueous emulsion useful in the

1 practice of the invention are those of polyvinyl acetate,
2 ethylene-vinyl acetate copolymer (having an ethylene
3 content of below 30%), acrylic esters, water-soluble shellac and the
4 like. Examples of polymers soluble in alcohol include
5 polyvinyl butyral, polyacrylamide, polyamide-epichloro-
6 hydrin, shellac, polyvinyl acetate and the like.
7 These resins are capable of forming films of relatively
8 good water proof after drying. The amount of these resins
9 vary depending on the type of resin and other factors
10 including the type and amount of filler and the thickness
11 of coating layer, but is generally in the range of 1 to 50
12 wt%, preferably 2 to 20 wt%, of a mixture of the resin and
13 PVP or PVP/VAc.

14 In addition to these resins, various additives may be
15 added to the PVP or PVP/VAc and filler. In particular, the
16 resistance or the fastness to light of recorded matter is
17 one of important problems to solve.

18 Then, we have made an intensive study on the light
19 fastness or resistance. The most general way of improving the fastness
20 to light of recorded matter is to use dyes which are
21 excellent in fastness to light. However, since inks to be
22 employed in the ink jet recording system are required not
23 to cause clogging of ink jet nozzles and to have a clear
24 color tone, dyes with excellent light fastness cannot always
25 be employed. Basic dyes, acid dyes, or mordant dyes are

1 clear in color tone and are now widely used for the ink jet
2 recording purpose but these dyes are not necessarily
3 excellent in light fastness.

4 The improvement of light fastness of recorded matter
5 can be realized by adding to the aqueous dispersion or
6 composition of PVP and/or PVP/VAc and filler (1)
7 antioxidants, (2) UV absorber and (3) metal oxides, metal
8 chlorides or tannic acid capable of reacting with dyes to
9 convert the dyes into light-fast dyes.

10 During the course of our study, we have found that
11 though the light fastness more or less depend on the type
12 of dye, the light fastness of recorded matter is poorer
13 than that of dye in liquid state and the fading is mainly
14 caused by photooxidation based on oxygen in air and light.
15 To prevent this, antioxidants have been found to be
16 effective. Moreover, an investigation was conducted
17 to know the mechanism of the fading in relation to wavelength.
18 That is, glass filters were used to select desired ranges of
19 wavelength and a Xenone fade meter was used to measure the
20 resistance to light of recorded matter. As a result, it
21 was found (1) that little fading took place in the wavelength
22 range of infrared rays, (2) that in the range of visible
23 light, fading occurred in a wavelength corresponding to a
24 main absorption peak of dye; (3) that fading by the
25 ultraviolet light was as great as in (2).

1 For instance, a magenta ink composed of 79% of
2 water, 20% of ethylene glycol and 11% of Basic Violet
3 showed light resistance as follows.

4		
5	Wavelength (mn)	<u>Lowering Rate of Excitation Purity</u>
6		Relative Value of Irradiation Energy
7		
8	250 - 320	2.32
9	320 - 380	1.25
10	440 - 520	0.97
11	520 - 620	2.42
12	Over 620	0.024

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14 From the results, it was considered that UV
15 absorbers were effective to prevent fading of recorded
16 matter, which was experimentally found ture.

17 These antioxidants, UV absorbers, and compounds
18 capable of converting dyes into light-resistant dyes or
19 pigments are used in amounts of 0.1 to 10 wt% of a mixture
20 of the PVP or PVP/VAc and filler. These additives are
21 discussed in examples.

22 Then, the present invention is particularly
23 described by way of examples, which should not be construed
24 as limiting the present invention.

25 It will be noted here that four types of PVP were

1 used having average molecular weights of 360,000
2 (hereinafter referred to as K-90), 160,000 (hereinafter
3 referred as K-60), 40,000 (hereinafter referred to as K-30)
4 and 10,000 (hereinafter referred to as K-10) but little or
5 no substantial difference in recording characteristics was
6 observed among them and K-30 was used as the representative
7 of PVP in examples. In addition, four types of PVP/VAc
8 having VP/VAc ratios of 70/39, 60/40, 50/50 and 30/70,
9 respectively, were used to check recording characteristics.
10 As a result it was found that good results were obtained in any
11 cases without showing any significant differences among
12 them. Accordingly, a PVP/VAc resin having a VP/VAc ratio
13 of 50/50 was used in examples as the representative for the
14 PVP/VAc.

15 The ink jet recording was carried out using an
16 On-demand-type head with a diameter of nozzle of 40 microns
17 in which three ink jetting heads were used to discharge
18 therefrom different types of inks including cyan, yellow and magenta.
19 By the combination of these inks, different colors of red,
20 green, blue and sepia were made. The discharge of ink was
21 changed in seven stages by controlling an application
22 voltage and the recording of 6 lines/mm was conducted. In
23 the case of monochrome, amounts of discharge per unit area
24 in the respective stages are 2.6×10^{-4} cc/cm² in first
25 stage, 4.7×10^{-4} cc/cm² in second stage, 6.4×10^{-4} cc/cm²

- 16 -

1 in third stage, 7.0×10^{-4} cc/cm² in fourth stage, 7.9×10^{-4}
2 cc/cm² in fifth stage, 8.7×10^{-4} cc/cm² in sixth stage,
3 and 9.4×10^{-4} cc/cm² in seventh stage, respectively. In
4 the case of blue in color, the amounts of discharge in the
5 respective stages become double and in the case of sepia
6 color, they become three times. Accordingly, the severest
7 recording conditions are those for the sepia color in the
8 seventh stage. Aside from these recordings, a recording of
9 2 lines/mm was also conducted for comparison.

10 Recorded matters were evaluated according to the
11 following measurements or observations: (1) Measurement of
12 optical density of the respective colors in the seventh
13 stage; (2) Judgement of a stage of sepia color where
14 inks start to run or spread so as to check a degree of
15 the running or spreading of the inks (which show a degree
16 of ink receptivity of paper); (3) Measurement of a time before the
17 sepia color of the seventh stage is apparently dried after
18 application thereof; and (4) Measurement of a rate of area
19 of recorded matter of the first stage in which two lines/mm
20 were recorded (to know a degree of spreading of ink dots or
21 a degree of so-called sharpness.

22 Example 1

23 In this example, calcium carbonate was used as a
24 white pigment and different types of binder resins were
25 used including PVP and PVP/VAc to be used in the present

1 invention.

2 To a 5% aqueous solution or dispersion of each
3 binder resin was added 15 wt% of calcium carbonate of a
4 powder form having a size of 0.1 to 0.2 microns, followed
5 by fan agitating to give a slurry. This slurry was applied
6 onto a commercially available groundwood paper by means of
7 a wire bar, followed by roll pressing to obtain a surface-
8 coated paper. The coated layer had a thickness of 5 to
9 20 microns, i.e. 0.3 - 2.0 g of the coating was applied
10 onto an A-4 size paper.

11 The respective recording papers thus made were
12 subjected to the recording procedure and evaluated
13 according to the measuring methods described hereinabove.
14 The test results are shown in Table 1.

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- 18 -

Table 1

Binder resin	Optical density	Stage where spreading starts to appear	Drying time (seconds)	Rate of area (%)
PVP	1.03	>7	<10	14.4
PVP/VAc	0.99	>7	<10	14.8
Oxydized starch	1.14	4	180	11.2
Polyacryl- amide	0.52	2	200	20.5
PVA	0.96	6	60	15.0
Sodium aluginate	0.83	4	180	20.1
Styrene- maleic acid copolymer	0.78	4	250	22.2
CMC	0.87	5	220	17.6
Casein	0.82	3	320	13.2
Soybean protein	0.72	3	300	14.6
Gelatin	0.83	5	240	21.5
SBR latex	0.69	4	450	18.9
Hydroxyethyl cellulose	0.85	6	80	18.2
Etherified starch	0.69	5	170	17.6

In this table, the optical density was determined

- 18 -

1 with respect to the magenta color of the seventh stage and
2 other six colors showed a similar tendency.

3 As will be clearly seen from the results of Table 1,
4 the binder resin gives a great influence on the
5 characteristics of ink spreading, drying time and the like and
6 the PVP/VAc resins involve no spreading or running at the
7 seventh stage and are thus much more excellent than the
8 other binder resins. PVA and hydroxyethyl cellulose rank
9 second to PVP and PVP/VAc with respect to optical
10 density but these resins were inferior in spreading
11 characteristic, i.e. spreading occurred at the
12 sixth stage, and required a drying time of as long as 60 to
13 80 seconds. As to the optical density and rate of area,
14 oxidized starch was excellent and PVP and PVP/VAc showed
15 such characteristics next to oxidized starch.

16 Example 2

17 In this example, PVP and PVP/VAc were used as a
18 binder resin and different types of white pigments were
19 used in combination for comparative purpose.

20 To a 10% aqueous solution of PVP or PVP/VAc was
21 added each of white pigments to be tested to give a slurry
22 in the same manner as in Example 1 and the slurry was
23 applied in the same manner as in Example 1 to obtain a
24 surface coated paper. The type and amount of white pigment
25 and the results of recorded matter are shown in Table 2
below with regard to the PVP binder resin.

Table 2

White pigment (amount by wt.)	Optical density	Stage where spreading starts to appear	Drying time (seconds)	Rate of area (%)	Whitely fading phenomenon
clay (20%)	1.11	6	15	13.7	no
talc (20%)	1.00	>7	<10	11.5	no
calcium carbonate (20%)	1.11	>7	<10	14.9	no
calcium sulfate (20%)	0.97	>7	<10	12.0	no
calcium silicate (10%)	0.97	>7	<10	10.4	no
diato- maceous earth (15%)	0.98	7	<10	16.5	no
aluminium hydroxide (20%)	0.92	7	14	13.9	no
titanium oxide (20%)	0.85	6	15	14.8	yes
silica (20%)	0.82	7	20	14.5	yes
aluminium silicate (20%)	0.87	7	20	10.9	yes
satin white (20%)	0.80	7	15	11.7	yes
zinc oxide (20%)	0.87	7	15	13.9	yes

1 As will be appreciated from the results of Table 2,
2 with titanium oxide, silica, aluminium silicate, satin
3 white and zinc oxide, there appears a whitely fading
4 phenomenon where an entirety of image is observed as white
5 and the optical density does not become higher than 0.9.
6 This is because an ink does not remain on the surface of
7 the coated paper and the white pigment deposits out on the
8 paper surface. In contrast thereto, clay, talc, calcium
9 carbonate, calcium sulfate, calcium silicate, diatomaceous
10 earth and aluminium hydroxide show no fading phenomenon
11 and optical densities of above 0.9. The white pigments
12 causing the fading phenomenon cannot be used in large
13 amounts and do not show an effect of increasing the whiteness
14 of paper though usable in the practice of the invention.
15 In this sense, the white pigments showing no fading
16 phenomenon are conveniently and preferably used. Preferable
17 pigments further include magnesium silicate, terra alba,
18 activated clay, magnesium oxide and magnesium carbonate.
19 As regards the spreading characteristic and drying time,
20 there is not a significant difference depending on the type
21 of pigment, revealing that such characteristics are mainly
22 dependent of the type of binder.

23 In Table 2, the binder used was PVP and similar
24 results were obtained when PVP/VAc was used except that the
25 optical density was reduced by about 0.5 in all the cases.

Example 3

In this example, PVP was used as binder resin and calcium carbonate, calcium silicate and talc were used as pigment to determine an effect of a ratio by weight of the binder and the white pigment on the recording characteristics. The coated paper was made in the same manner as in Example 1. In Table 3, there are shown results of a test using calcium carbonate.

Table 3

PVP (%)	Calcium carbonate	Optical density	Stage where spreading starts to appear	Drying time (seconds)	Rate of area (%)	Whitely fading phenomenon
2	20	0.85	7	15	14.8	yes
5	20	0.98	>7	<10	16.3	no
10	20	1.11	>7	<10	13.0	no
15	20	1.19	>7	<10	12.2	no
20	20	1.24	>7	<10	6.5	no
20	15	1.12	>7	<10	9.7	no
20	10	0.97	>7	<10	11.6	no
20	5	0.84	>7	<10	14.8	no
20	2	0.75	>7	<10	20.0	no
20	1	0.58	>7	<10	32.0	no

1 As will be clear from the results of Table 3, high
2 optical density cannot be obtained when amounts of PVP
3 and calcium carbonate are too great or too small. That is,
4 in order to obtain good recording characteristics, a
5 PVP/calcium carbonate (with an average size of 0.1 to 0.2
6 microns) ratio by weight is preferably in the range of 10 :
7 1 to 0.25 : 1. When a similar test was conducted using a
8 calcium silicate powder having an average particle size of
9 0.1 micron and a talc powder having an average size of 0.2
10 to 0.3 microns, it was found that a preferable weight ratio
11 was in the range of 10 : 1 to 0.5 : 1 for calcium silicate
12 and 5 : 1 to 0.2 : 1 for talc. The weight ratio is, of
13 course, dependent on the size of white pigment and the
14 weight ratio of PVP or PVP/VAc and a white pigment is
15 conveniently in the range of 10 : 1 to 0.2 : 1.

16 Furthermore, when the composition comprising calcium
17 carbonate and PVP was applied in different thicknesses
18 ranging from 4 microns to 28 microns, no significant
19 difference in recording characteristics was found in this
20 range of thicknesses.

21 In addition, four types of paper support showing
22 different water absorptivities were used to check their
23 influence on the recording characteristics. As a result,
24 it was found that when the coated layer had a thickness of
25 above 8 microns, inclusive, good results were obtained in

1 any cases.

2 From the above, the coated layer should preferably
3 have a thickness of 8 microns or more, and the coating com-
4 position of the invention can be widely applied to a wide
5 variety of paper supports.

6 Example 4

7 In this example, PVP and other binder resins were
8 used in combination. As a white pigment, talc (Chinese
9 talc) were used. Amounts of the binder resin and talc
10 were, respectively, 20%. Coated papers were made
11 substantially in the same manner as in Example 1, with the
12 results summarized in Table 4 below.

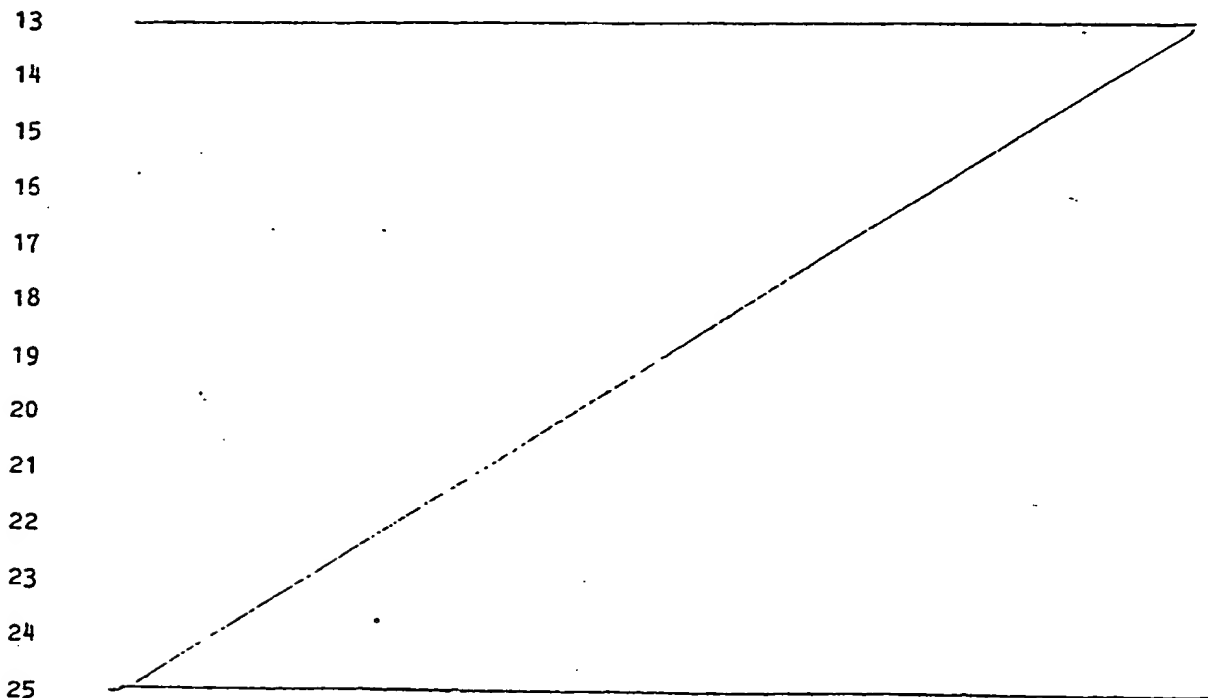


Table 4

Binder resin	Weight ratio	Optical density	Stage where spreading starts appear	Drying time (seconds)	Rate of area (%)
PVP/PVA	1/1	0.94	>7	<10	12.9
PVP/PVA	1/2	0.94	>7	13	12.5
PVP/PVA	1/5	0.92	7	40	12.7
PVP/oxidized starch	1/1	1.10	>7	24	10.4
PVP/oxidized starch	1/2	1.06	7	53	11.8
PVP/oxidized starch	1/5	0.92	6	190	13.0
PVP/styrene-maleic copolymer	1/1	0.86	7	50	15.5
PVP/styrene-copolymer	1/2	0.86	7	62	16.9
PVP/styrene-copolymer	1/5	0.89	5	280	22.0
PVP/-hydroxyethyl cellulose	1/1	0.93	>7	18	13.7

As will be appreciated from the above results, binder resins such as PVA, oxidized starch and the like show more excellent ink receptivity when applied in combination with PVP.

A greater amount of PVP is desirable in view of the

1 ink receptivity. Though the content of PVP depends on the
 2 type of the second binder, it is in the range of over 20 wt%
 3 when the binder resin used in combination with PVP shows
 4 water absorptivity such as PVA and in the range of 33 wt%
 5 when the second binder resin shows no water absorptivity.

6 Example 5

7 In this example, characteristics of ink jet
 8 recording papers made by a size press technique are
 9 described.

10 Different types of binder and calcium carbonate were
 11 mixed in a ratio of 1:1 in an aqueous medium to obtain 10%
 12 slurries. Each slurry was coated on a commercially
 13 available groundwood paper by a size press system to obtain
 14 a surface coated paper with a coating spread of 4.0 g/m².
 15 The results are shown in Table 5 below.

Table 5

Binder resin	Weight ratio	Optical density	Stage where spreading starts appear	Drying time (seconds)	Rate of area (%)
PVP		1.18	>7	<10	11.0
PVP/VAc		0.98	>7	<10	13.0
PVP/PVA	1/1	0.96	>7	18	14.7
PVP/-oxidized starch	1/1	1.14	7	20	12.5

1 From the above results, it will be seen that the
2 characteristics of the recording papers made by the size
3 press technique are substantially the same as those of the
4 recording papers obtained by the wire bar. For instance,
5 the recording paper of the coated type using PVP/VAc as
6 binder had an optical density of 0.99, a spreading stage
7 of >7, a drying time of <10, and a rate of area of <10 as
8 shown in Table 1, which are almost the same as those of
9 Table 5. In the PVP/PVA and PVP/oxidized starch systems,
10 the recording characteristics are almost the same as those
11 of Table 4. Accordingly, the size press technique can be
12 used similarly with the surface coating method.

13 Example 6

14 In this example, binder resins and calcium carbonate
15 used as white pigment were applied internally or mixed with
16 pulp.

17 LBKP and NBKP were mixed in a ratio of 1 : 2 and
18 beaten in a refiner. Then, light calcium carbonate was
19 added to the pulp in an amount of 30 parts by weight per
20 100 parts by weight of the pulp and PVP or PVP/VAc was
21 added in an amount of ranging from 0.5 to 30 wt% based on
22 the pulp. The pulp composition was subjected to a
23 paper-making process using a Fourdriner test machine to
24 make a paper with a basis weight of 70 g/m². The thus made
25 papers were each subjected to the calender rolls to give

recording papers.

The recording papers were applied with inks and evaluated in the same manner as described hereinbefore, with the result shown in Table 6 below.

Table 6

Binder resin	Amount (%)	Optical density	Stage where spreading starts to appear	Drying time (seconds)	Rate of area (%)
PVP	0.5	0.80	6	15	19.3
PVP	1	0.85	7	10	17.5
PVP	2	0.96	>7	<10	15.6
PVP	5	0.98	>7	<10	15.4
PVP	10	1.00	>7	<10	15.0
PVP	20	1.00	>7	<10	15.1
PVP	30	1.01	>7	<10	15.3
PVP/VAc	0.5	0.72	5	20	20.1
PVP/VAc	1	0.82	6	15	17.9
PVP/VAc	2	0.92	7	10	16.1
PVP/VAc	5	0.95	>7	10	16.0
PVP/VAc	10	0.98	>7	<10	15.9
PVP/VAc	20	0.98	>7	<10	15.9
PVP/VAc	30	0.98	>7	<10	15.5

1 In the table, the optical density is obtained -
2 from the magenta color of the seventh stage and as regards
3 the other six colors, a similar tendency is observed.

4 As will be appreciated from the above results, where
5 the binder content is 0.5% or 1%, the optical density,
6 stage where spreading appeared, drying time and rate of
7 area are not satisfactory. Accordingly, the binder resin
8 should be contained in an amount of at least 2% of the
9 pulp. This is much larger as compared with an amount of an
10 strength improver ordinarily employed in the paper-making
11 industry (generally in the range of 0.2 to 1 wt%). On the
12 other hand, the recording papers in which 30% of PVP or
13 PVP/VAc based on the pulp is contained show excellent
14 recording characteristics but become sticky to the touch.
15 In addition, such papers show a blocking tendency.

16 Gathering the above, the content of PVP or PVP/VAc
17 is in the range of 2 wt% to 20 wt% of the pulp.

18 Example 7

19 In this example, an amount of PVP was set at 10% by
20 weight of pulp but an amount of calcium was changed.
21 Recording papers were each made and evaluated in the same
22 manner as in Example 6. The test results are shown in Table
23 7 below.

24

25

- 30 -

Table 7

White filler	Amount (%)	Optical density	Stage where spreading starts to appear	Drying time (seconds)	Rate of area (%)
calcium carbonate	3	0.83	7	20	21.0
"	5	0.91	7	15	16.5
"	10	0.96	>7	<10	15.2
"	20	1.01	>7	<10	14.9
"	40	1.00	>7	<10	15.0
"	50	0.97	>7	<10	14.1
"	60	0.83	>7	<10	12.4
"	70	0.45	>7	<10	10.3

As will be apparent from the above results, good recording characteristics are obtained when the content of the white filler is in the range of 10 to 60 wt% of the pulp. Less contents are disadvantageous in that the optical density is poor while larger contents lead to the whitely fading phenomenon. Accordingly, an effective amount of calcium carbonate is in the range of 10 to 60 wt% of the pulp. In this connection, the content of calcium carbonate more or less depends on the content of PVP, e.g. when the content of PVP is 2%, the upper limit in content of calcium carbonate was found to be 40%. Similar

1 results were obtained when PVP/VAc was used instead of PVP.

2 The above procedure was repeated using other several
3 white pigments in different amounts. As a result, it was
4 found that a suitable content of clay was in the range of
5 10 to 60 wt% of the pulp, that of talc ranged from 10 to 60
6 wt%, that of calcium sulfate ranged from 5 to 40 wt%, that
7 of calcium silicate ranged from 10 to 40 wt%, that of
8 diatomaceous earth ranged from 10 to 60 wt%, that of satin
9 white ranged from 5 to 50 wt%, and that of zinc oxide
10 ranged from 15 to 40 wt%. Generally speaking, white
11 pigments are effectively usable in the range of 10 to 60
12 wt% of pulp. Other usable white pigments in this internal
13 application technique are aluminium hydroxide, silica,
14 aluminium silicate, magnesium silicate, terra abla,
15 activated clay, magnesium oxide, magnesium carbonate,
16 aluminium oxide and the like. Among the white pigments,
17 preferable ones are those mentioned with respect to the
18 surface coating method.

19 The following three examples illustrate water-proof,
20 film-forming resins added to the basic composition used in
21 the present invention.

22 Example 8

23 In this example, binder resin made of 90 parts by
24 weight of PVP and 10 parts by weight of different types of
25 film-forming polymers were used.

1 To 10% aqueous or alcoholic solutions of various
2 binder resin mixtures was added calcium carbonate powder
3 with a size of 0.1 to 0.2 microns in an amount of as great
4 as three times the binder resin mixture, followed by
5 agitating with a fan to give slurries. Each slurry was
6 applied onto a commercially available groundwood paper by a
7 wire bar and the thus applied paper was roll pressed to
8 obtain surface coated papers. The thickness of the coated
9 layer was in the range of 5 to 20 microns. The thus
10 obtained papers were recorded and evaluated in the same
11 manner as in Example 1 except for water proof. That is,
12 the water proof was evaluated as follows: a time before
13 the coated layer was completely separated from a coated
14 paper specimen with a size of 1 cm x 2 cm after having
15 immersed the coated paper vertically in water was measured.
16 The test results are shown in Table 8 below.

Table 8

Binder resin mixture	Optical density	Stage where ink spreading starts to appear	Drying time (seconds)	Rate of area (%)	Water proof
PVP	1.03	>7	<10	14.4	5
PVP/VAc	0.99	>7	<10	14.8	5
PVP+oxidized starch	1.11	>7	14	10.0	7
PVP+PVA	1.00	>7	10	12.2	5
PVP+hydroxyethyl cellulose	0.98	>7	12	13.1	5
PVP+polyvinyl acetate	0.95	7	15	14.5	25
PVP+ethylene/vinyl acetate copolymer	0.94	7	19	13.9	30
PVP+acrylic ester resin	0.97	7	17	13.9	25
PVP+water-soluble shellac	1.01	7	13	12.8	40
PVP+ polyvinyl butyral*	0.98	7	15	14.5	35
PVP+polyacrylamide*	0.95	7	14	14.3	20
PVP+polyamide·epi-chlorohydrin*	0.93	7	14	13.9	25
PVP+ shellac*	1.00	7	13	14.5	60

* Note: These resins were dissolved in methanol.

1 From the above results, it will be appreciated that when
2 PVP or PVP/VAc is used singly, the water proof is 5 seconds
3 or less. In addition, systems of PVP or PVP/VAc to which
4 other water-soluble polymers such as oxidized starch, PVA
5 and hydroxyethyl cellulose have been added show a slight
6 improvement in water proof. On the other hand, binder
7 resin mixtures in which 10 wt% of aqueous emulsion-type
8 polymers such as polyvinyl acetate, ethylene-vinyl acetate
9 copolymer, acrylic ester resin and water-soluble shellac show a
10 water proof of over 25 seconds, thus improving the water
11 proof remarkably. These binder resin mixtures are
12 slightly inferior in recording characteristics, i.e. the
13 spreading stage of seven and a drying time of 13 - 19, to
14 the PVP or PVP/VAc resin alone. However, these slight
15 degrees of deterioration of the characteristics are almost
16 negligible and the improvement in water proof is much more
17 effective. Similar results are obtained when polyvinyl
18 butyral, polyacrylamide, polyamide-epichlorohydrin, shellac
19 and the like are used as dissolved in methanol solvent.

20 Aside from the resins mentioned above, other resins
21 are also usable in combination with PVP and/or PVP/VAc
22 including vinyl acetate-acrylonitrile copolymer, styrene
23 resin, styrene-acrylonitrile copolymer, methacrylic ester
24 resin, polyamide resin, melamine resin, melamine-urea resin
25 and the like.

Example 9

In this example, an influence of polyvinyl acetate in a binder resin composed of PVP and polyvinyl acetate was checked. To an aqueous 10% solution of the binder resin was added talc (Chinese talc) in an amount of two times the binder resin to give a slurry. Then, Example 8 was repeated with the results shown in Table 9.

Table 9

Binder resin	Weight ratio	Optical density	Stage where spreading starts to appear	Drying time (sec)	Rate of area (%)	Water proof
PVP/poly-vinyl acetate	98/2	1.04	7	10	14.7	5
"	95/5	1.02	7	12	14.3	18
"	90/10	0.97	7	15	14.8	25
"	80/20	0.98	7	19	14.2	33
"	60/40	0.95	7	20	14.2	45
"	50/50	0.95	6	23	14.7	60
"	40/60	0.93	5	49	15.2	100
"	20/80	0.93	5	125	16.6	120

1 As will clear from the above results, the proof to
2 water is more improved as the amount of polyvinyl acetate
3 is increased. However, the optical density, spreading
4 characteristic and drying time become more deteriorated
5 with an increasing amount of polyvinyl acetate. For
6 instance, the drying time is 49 seconds for the binder
7 system of PVP/polyvinyl acetate = 40/60. This time is
8 longer than a time of from completion of image formation
9 till withdrawal of the recorded matter from a machine and
10 is not thus practical. Taking the above into
11 consideration, a maximum amount of polyvinyl acetate should
12 be 50%, i.e. it is necessary that polyvinyl acetate does
13 not exceed that of PVP. On the other hand, the binder
14 system containing 2% of polyvinyl acetate does show little
15 effects and thus polyvinyl acetate should be over 2%.

16 The above procedure was repeated using different
17 types of film-forming and water-proof polymers to determine
18 the range of addition of each polymer which may more or
19 less depend on the type and amount of white pigment, and
20 thickness of the coated layer. The results are shown in
21 Table 10.

- 37 -

Table 10

Binder resin	Possible range of addition
PVP/ethylene-vinyl acetate copolymer	98/2 - 60/40 on a weight basis
PVP/acrylic ester resin	98/2 - 60/40
PVP/water shellac	99/1 - 70/30
PVP/polyvinyl butyral	99/1 - 70/30
PVPpolyacrylamide	99/1 - 70/30
PVP/polyamide·epichlorohydrin	99/1 - 60/40
PVP/shellac	99/1 - 70/30
PVP·VAc/polyvinyl acetate	98/2 - 50/50
PVP·VAc/ethylene-vinyl acetate copolymer	98/2 - 60/40
PVP·VAc/acrylic ester resin	98/2 - 60/40
PVP·VAc/water shellac	99/1 - 70/30
PVP·VAc/polyvinyl butyral	99/1 - 70/30
PVP·VAc/polyacrylamide	99/1 - 70/30
PVP·VAc/polyamide·epichlorohydrin	99/1 - 60/40
PVP/shellac	99/1 - 70/30

From the above results, it is generally possible to use these water proof-imparting resins in the range of 1 to 50 wt% of the mixture with PVP or PVP/VAc provided that the type and amount of white pigment and the thickness of the coated layer are properly controlled.

Example 10

In this example, characteristics of ink jet

recording papers made by the size press technique are shown.

Various binders (PVP : additive polymer = 90 : 10) and calcium carbonate were mixed in a weight ratio of 1 : 2 to give 10% slurries. Each slurry was applied onto a commercially available groundwood paper by the size press method in an amount of 4.0 g/m² on a dry basis to give a surface coated paper. The thus obtained coated papers had recording characteristics shown in Table 11.

Table 11

Binder resin	Optical density	Stage where ink spreading starts to appear	Drying time (seconds)	Rate of area (%)	Water proof (seconds)
PVP	1.04	7	10	14.2	5
PVP/VAc	1.00	7	10	14.6	5
PVP/poly-vinyl acetate	0.95	7	14	14.3	31
PVP/-acrylic ester resin	0.98	7	20	14.0	23
PVP/poly-vinyl butyral	0.97	7	15	14.3	40
PVP/water shellac	1.01	7	15	13.0	45
PVP/ethyl-ene-vinyl acetate copolymer	0.94	7	18	14.5	35
PVP VAc/-polyvinyl acetate	0.93	7	17	14.8	40

1 As will be clearly seen from the above results, the
2 characteristics of the recording papers made by the size
3 press method are excellent similarly to those of the
4 recording papers made by the wire bar coating method. As
5 for the water proof, the recording papers made by the size
6 press method are slightly superior to those obtained by the
7 wire bar coating method. Thus, the size press technique
8 can be used similarly with the surface coating method.

9 The following examples deal with the manner of
10 imparting light resistance to recorded matter in which
11 antioxidants, Ultraviolet absorbers and compounds capable
12 of reacting with dyes for conversion into light-resistant
13 dyes.

14 The measurement of light resistance was conducted
15 according to a method as prescribed in JIS L0843-71 using a
16 2.5 KW xenon fade meter of an air-cooling type (made by
17 Suga Tester K.K.). The irradiation energy was 464
18 J/cm²·Hr, which is 9.6 times that of an average sunlight
19 and 380 times that of a fluorescent lamp.

20 The ink jet recording was carried out using an
21 On-demand-type head having a nozzle diameter of 40 microns
22 and a voltage of 200 V was applied to the recording system.

23 When a recording of 6 lines/mm² was effected, a discharge
24 per unit area was 7.9×10^{-4} cc/cm².

25 Recording papers used were made by applying onto a

1 commercially available high quality paper three types of
2 coating composition comprising three types of binders of
3 polyvinyl alcohol, oxidized starch/polyvinyl alcohol
4 (30/70) and polyvinyl alcohol/polyvinylpyrrolidone (40/60)
5 and calcium carbonate as white filler in a binder-to-filler
6 ratio of 1 : 1, respectively. The coating amount was 40
7 g/m². The three types of recording papers were designated
8 as recording papers A, B and C respectively. Antioxidants,
9 UV absorbers and the specific type of compounds capable of
10 reacting with dyes were dissolved in binder to make
11 recording papers. It will be noted that these additives
12 are effective for any recording papers which are to be
13 applied with dyes for recording purpose and application of
14 these additives to recording papers outside the scope of
15 the invention is also described in the following examples
16 to evidence the excellency of these additives.

17 Example 11

18 Various metal oxides and organic acids were added to
19 the binders in such an amount that they were contained in
20 the surface coating in an amount of 0.5 g/m². Then,
21 recording papers were made substantially in the same manner
22 as in the foregoing examples.

23 Then, a magenta ink made of 79% by weight of water,
24 20% by weight of ethylene glycol and 1% by weight of C.I.
25 Basic Violet 10 was prepared and used for recording on the
26 respective recording papers. The recorded papers were

1 irradiated for 12 hours in the xenone fade meter and their
 2 optical density was measured. The test results are
 3 shown in Table 12 below.

Table 12 (1)

Rec- ording paper	Additive	Optical Density (O.D.)		
		Irradiation time (0 hour)	Irradiation time (12 hours)	O.D.(12 hours)/ O.D.(0 hors)
A	nil	0.93	0.41	0.44
A	phosphorus tungstic acid	0.84	0.68	0.81
A	phosphorus molybdic acid	0.89	0.82	0.92
A	phosphorus tungsten molybdic acid	0.91	0.88	0.97
A	chromic chloride	0.88	0.83	0.94
A	tannic acid	0.99	0.99	1.00
B	nil	0.97	0.42	0.43
B	phosphorus tungstic acid	0.91	0.78	0.92
B	phosphorus molybdic acid	0.93	0.86	0.92
B	phosphorus tungsten molybdic acid	0.96	0.90	0.94
B	chromic chloride	0.89	0.84	0.94

- 42 -

Table 12 (2)

Rec- ording paper	Additive	Optical Density (O.D.)		
		Irradiation time (0 hour)	Irradiation time (12 hours)	O.D. (12 hours) / O.D. (0 hours)
B	tannic acid	0.99	0.98	0.99
C	nil	0.88	0.35	0.40
C	phosphorus tungstic acid	0.85	0.62	0.73
C	phosphorus molybdic acid	0.88	0.81	0.92
C	phosphorus tungsten molybdic acid	0.87	0.82	0.94
C	chromic chloride	0.81	0.76	0.94
C	tannic acid	0.92	0.82	0.89

As will be seen from the above results, the additives are found to remarkably improve the light resistance of recorded matter. In practice, the phosphorus-containing acids are preferably used because of their excellency in color retentivity.

Example 12

Various inks composed of 76 to 79 % by weight of water 20 % by weight of ethylene glycol and 1 to 4 % by weight of different types of dyes were made and applied on a recording paper D which was made by applying 0.5 g/m² of phosphorus molybdic acid to the recording paper A and a

recording paper E applied with 0.5 g/m^2 of tannic acid similarly to the case of the recording paper D.

The light resistance was measured in the same manner as in Example 11 with the results shown in Table 13 below.

Table 13 (1)

Rec- ording paper	Dye	Optical Density (O.D.)		
		Irradiation time (0 hour)	Irradiation time (12 hours)	O.D. (12 hours) / O.D. (0 hour)
A	C.I. Basic Yellow 11	0.57	0.39	0.69
D	"	0.59	0.49	0.83
E	"	0.61	0.52	0.85
A	C.I. Basic Red 1	0.79	0.35	0.44
D	"	0.77	0.53	0.69
E	"	0.71	0.51	0.72
A	C.I. Basic Red 3	0.78	0.56	0.72
D	"	0.75	0.54	0.85
E	"	0.74	0.62	0.84
A	C.I. Basic Violet 14	0.97	0.37	0.38
D	"	0.91	0.63	0.69
E	"	0.93	0.69	0.75

Table 13 (2)

Recording paper	Dye	Optical Density (O.D.)		
		Irradiation time (0 hour)	Irradiation time (12 hours)	O.D.(12 hours)/ O.D.(0 hour)
A	C.I. Basic Blue 3	0.79	0.46	0.58
D	"	0.77	0.57	0.74
E	"	0.73	0.55	0.77
A	C.I. Mordant Orange 4	0.41	0.30	0.73
D	"	0.39	0.30	0.77
E	"	0.42	0.32	0.77
A	C.I. Mordant Red 15	0.77	0.59	0.77
D	"	0.72	0.61	0.85
E	"	0.75	0.67	0.89
A	C.I. Mordant Violet 5	0.71	0.62	0.87
D	"	0.73	0.67	0.92
E	"	0.68	0.62	0.91
A	C.I. Mordant Black 7	0.82	0.75	0.91
D	"	0.79	0.75	0.95
E	"	0.83	0.78	0.94
A	C.I. Acid Yellow 17	0.51	0.21	0.41
D	"	0.53	0.44	0.83
E	"	0.52	0.47	0.90

- 45 -

Table 13 (3)

Recording paper	Dye	Optical Density (O.D.)		
		Irradiation time (0 hour)	Irradiation time (12 hours)	O.D.(12 hours)/ O.D.(0 hour)
A	C.I.Acid Orange 7	0.63	0.42	0.69
D	"	0.63	0.49	0.78
E	"	0.63	0.58	0.92
A	C.I.Acid Red 88	0.80	0.38	0.47
D	"	0.82	0.63	0.77
E	"	0.78	0.70	0.89
A	C.I.Acid Violet 49	0.92	0.32	0.35
D	"	0.95	0.71	0.75
E	"	0.90	0.75	0.83
A	C.I.Acid Blue 7	0.81	0.72	0.88
D	"	0.80	0.77	0.96
E	"	0.83	0.81	0.98
A	C.I.Acid Black 2	1.00	0.83	0.83
D	"	1.03	0.98	0.95
E	"	1.03	1.02	0.99
A	C.I.Acid Black 31	0.94	0.86	0.91
D	"	0.93	0.91	0.98
E	"	0.95	0.94	0.99

- 45 -

1 From the above results, it will be seen that the
2 phosphorus molybdic acid and tannic acid showed a very
3 remarkable effect of light resistance on the basic dyes and
4 acid dyes and a fair effect on the mordant dyes. However,
5 little effects on the direct dyes and disperse dyes were
6 recognized.

7 In these examples 11 and 12, five compounds are
8 illustrated and other effective additives includes halides
9 and oxides of at least one metal such as of barium,
10 manganese, iron, copper, calcium, magnesium, cobalt and
11 nickel.

12 The amount of these additives varies depending on
13 the type thereof but is generally in the range of 0.1 to
14 10% by weight of the coating composition in case of the
15 surface-coated recording paper. Larger amounts give an
16 adverse effect on the recording characteristics.

17 As will be appreciated from the results of Example
18 11, the additives show their light-resistant effect
19 independently of the type of coating. Further, their
20 effect is also developed when the additives are
21 incorporated in paper or applied by dipping paper in
22 solutions of the additives. This is particularly described
23 in Example 13 and 14.

24 Example 1

25 A commercially available high quality paper showing

a relatively high degree of water absorptivity was used on which recording was conducted by an ink jet recording technique using an ink as used in Example 11. After completion of the recording, the recorded matter was dipped in acetone or methanol solutions of 2 wt% of phosphorus tungstic acid, phosphorus molybdic acid, phosphorus tungsten molybdic acid, chromic chloride and tannic acid, then dried, and subjected to the measurement of light resistance. The results are shown in Table 14.

Table 14

Optical Density (O.D.)			
Additive	Irradiation time (0 hour)	Irradiation time (12 hours)	D.C. (12 hours)/ D.C. (0 hours)
nil	0.88	0.40	0.45
phosphorus tungstic acid	0.91	0.66	0.73
phosphorus molybdic acid	0.83	0.76	0.92
phosphorus tungsten molybdic acid	0.88	0.85	0.97
chromic chloride	0.83	0.79	0.97
tannic acid	0.95	0.93	0.98

- 48 -

1 These additives can improve the light resistance of
2 recorded matter when applied by the dipping method as will
3 be seen from the above results.

4 Example 14

5 LBKP having a freeness (C.S.F) of 400 ml was used as
6 stock pulp to which were added 10 wt% of talc, 0.2 wt% of a
7 wet strength improver and 0.5 wt% of additives each based
8 on the solid component of pulp. The thus added pulps were
9 each used to make papers with a basis weight of 50 g/m² in
10 a usual manner.

11 Then, an ink with the same composition as used in
12 Example 13 was used to record on the thus made papers and
13 the recorded matters were subjected to the measurement of
14 light resistance. The results are shown in Table 15 below.

- 48 -

- 49 -

Table 15

Additive	Optical Density (O.D.)		
	Irradiation time (0 hour)	Irradiation time (12 hours)	D.C. (12 hours)/ D.C. (0 hours)
nil	0.82	0.40	0.49
phosphorus tungstic acid	0.86	0.68	0.79
phosphorus molybdic acid	0.79	0.77	0.97
phosphorus tungsten molybdic acid	0.84	0.80	0.95
chromic chloride	0.79	0.71	0.90
tannic acid	0.91	0.89	0.98

The additive-incorporated papers show improved light resistance over the additive-free paper.

Example 15

Example 11 was repeated using various antioxidants, with the results shown in Table 16 below, in which the three recording papers are indicated as A', B' and C' corresponding to recording papers A, B and C of Example 11.

- 50 -

Table 16 (1)

Recording paper	Antioxidant	Optical density -		
		Irra- diation time (0 hr)	Irra- diation time (12 hrs)	O.D.(12 hrs)/ O.D.(0 hr)
A'	nil	0.93	0.41	0.44
"	hydroquinone	0.95	0.95	1.00
"	hydroquinon dimethyl ether	0.97	0.70	0.72
"	butylhydroxyanisole	0.93	0.82	0.88
"	p-tert-butylphenol	0.97	0.65	0.67
"	p-tert-butylcatechol	0.97	0.97	1.00
"	2,6-di-tert-butyl- phenol	1.00	0.98	0.98
"	2,6-tert-butyl-p- cresol	0.99	0.57	0.57
"	methylhydroquinone	0.92	0.85	0.92
"	2,2'-azobis- isobutyronitrile	0.87	0.53	0.61
"	benzotriazole	0.94	0.43	0.46
"	diphenylamine	0.94	0.73	0.78
"	1,1-diphenyl-2- picrylhydrazine	1.01	0.84	0.83
"	pyrogallol	0.94	0.84	0.89
B'	nil	0.97	0.42	0.43
"	hydroquinone	0.99	0.97	0.98
"	hydroquinone dimethyl ether	1.00	0.69	0.69
"	butylhydroxyanisole	0.99	0.84	0.85

- 50 -

- 51 -

Table 16 (2)

Recording paper	Antioxidant	Optical density -		
		Irra- diation time (0 hr)	Irra- diation time (12 hrs)	O.D.(12 hrs)/ O.D.(0 hr)
B'	p-tert-butylphenol	1.04	0.75	0.72
"	p-tert-butylcatechol	1.07	1.03	0.96
"	2,6-di-tert-butylphenol	1.05	1.03	0.98
"	2,6-di-tert-butyl-p-cresol	1.06	0.66	0.62
"	methylhydroquinone	0.98	0.95	0.97
"	2,2'-azobis-isobutyronitrile	0.89	0.64	0.72
"	benzotriazole	1.03	0.49	0.48
"	diphenylamine	1.01	0.81	0.80
"	1,1-diphenyl-2-picryl-hydrazine	1.09	0.93	0.85
"	pyrogallol	1.00	0.91	0.91
C'	nil	0.88	0.35	0.40
"	hydroquinone	0.92	0.90	0.98
"	hydroquinone dimethyl ether	0.96	0.69	0.72
"	butylhydroxyanizole	0.91	0.80	0.88
"	p-tert-butylphenol	0.95	0.60	0.63
"	p-tert-butylcatechol	0.90	0.89	0.99
"	2,6-di-tert-butylphenol	0.97	0.95	0.98

- 51 -

Table 16 (3)

Recording paper	Antioxidant	Optical density		
		Irra- diation time (0 hr)	Irra- diation time (12 hrs)	O.D. (12 hrs) / O.D. (0 hr)
C'	2,6-di-tert-butyl- p-cresol	0.97	0.47	0.48
"	methylhydroquinone	0.90	0.75	0.83
"	2,2'-azobis- isotutyronitrile	0.81	0.43	0.53
"	benzotriazole	0.91	0.38	0.42
"	diphenylamine	0.88	0.50	0.57
"	1,1-diphenyl-2- picrylhydrazine	0.97	0.76	0.78
"	pyrogallol	0.91	0.81	0.89

These results reveal that the addition of antioxidants can remarkably improve the light resistance. The degree of the improvement more or less depends on the type of antioxidant and hydroquinone, p-tert-butylcatechol, 2,6-di-tert-butylphenol and methylhydroquinone are particularly excellent in improving the light resistance.

Aside from those mentioned above, there are usable styrenated phenol, 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), 2,2'-thiobis(4-methyl-6-t-butylphenol), alkylthiodi propionates,

1 2-mercaptobenzoimidazole, N-n-butyl-p-aminophenol, phenyl-
2 enediamines, α -naphthylamine, N-phenyl- α -naphthylamine,
3 N,N'-disalicylidene-1,2-propylenediamine, phenothiazine,
4 tris(nonylphenyl)phosphite, triphenylphosphite, tris(3,5-
5 di-t-butyl-4,4-hydroxyphenylphosphate, dithiocarbamate,
6 anthogenate, dihydroquinoline derivatives, mercaptobenzi-
7 midazoles, monoisopropyl citrate, ethyl protocathecuete,
8 alkyl gallates, nordihydroguaiaretic acid, L-sorbic acid,
9 and the like.

10 Example 16

11 Various inks composed of 77 to 79 wt% of water, 20%
12 by weight of ethylene glycol and 1 to 3% by weight of
13 different types of dyes were made and applied on a
14 recording paper D' which was made by incorporating 0.5 g/m²
15 of methylhydroquinone in the recording paper A'. The light
16 resistance was measured in the same manner as in Example
17 15. The results are shown in Table 17 below.

- 54 -

Table 17

Recording paper	Dye	Optical Density (O.D.)		
		Irradiation time (0 hr)	Irradiation time (12 hrs)	O.D.(12 hrs)/ O.D.(0 hr)
D'	C.I. Basic Violet 14	0.95	0.90	0.95
A'	"	0.97	0.37	0.38
D'	C.I. Basic Blue 3	0.79	0.73	0.92
A'	"	0.79	0.46	0.58
D'	C.I. Basic Yellow 11	0.53	0.51	0.97
A'	"	0.57	0.39	0.69
D'	C.I. Basic Red 1	0.78	0.69	0.89
A'	"	0.79	0.35	0.44
D'	C.I. Basic Red 13	0.77	0.75	0.97
A'	"	0.78	0.56	0.72
D'	C.I. Acid Yellow 17	0.57	0.52	0.92
A'	"	0.51	0.21	0.81
D'	C.I. Acid Orange 7	0.61	0.47	0.77
A'	"	0.63	0.43	0.69
D'	C.I. Acid Red 88	0.82	0.57	0.70
A'	"	0.80	0.38	0.47

- 54 -

1 From the above results, it will be seen that though
2 an influence of the antioxidants on the light resistance
3 varies depending on the type of dye, good results are
4 obtained in all the cases. Accordingly, the addition of
5 antioxidant is believed effective in improving the light
6 resistance by application to various types of dye.

7 The amount of the antioxidants also varies depending
8 on the type but is generally in the range of 0.1 to 10% by
9 weight of the coating composition when such composition is
10 applied by the surface coating technique. Larger amounts
11 give an adverse effect on the recording characteristics.

12 The antioxidants can also be applied by dipping
13 paper in solutions of antioxidants or internally
14 incorporated paper. This is particularly described in
15 examples which follow.

16 Example 17

17 A commercially available high quality paper showing
18 a relatively high degree of water absorptivity was used and
19 an ink jet recording using an ink of C.I. Basic Violet 10
20 was conducted on such paper. The recorded paper was then
21 dipped an acetone solution of each of antioxidants (2 wt%)
22 for 2 seconds. After drying, the light resistance of the
23 dipped paper was measured using the xeon fade meter. The
24 results are shown in Table 18 below.

- 56 -

Table 18

Antioxidant	Optical Density (O.D.)		
	Irradiation time (0 hour)	Irradiation time (12 hours)	O.D. (12 hrs)/ O.D. (0 hr)
nil	0.91	0.38	0.42
hydroquinone	0.91	0.89	0.98
p-tert-butylcatechol	0.93	0.92	0.99
2,2-di-tert-butylphenol	0.93	0.90	0.97
methylhydroquinone	0.88	0.86	0.98
butylhydroxyanisole	0.88	0.83	0.94
diphenylamine	0.90	0.79	0.88
pyrogallol	0.89	0.80	0.90

As will be seen from the above results, the dipping method is also effective in improving the light resistance similarly to the surface coating method.

Example 18

LBKP having a freeness (C.S.F) of 400 ml was used as starting pulp to which were added 10 wt% of talc, 2 wt% of a wet strength improver and 0.5 wt% of antioxidants each based on the solid component of pulp. The thus added pulps were each used to make papers with a basis weight of 50 g/m² in a usual manner.

1 Then, an ink with the same composition as used in
2 Example 17 was used and applied on the thus made papers,
3 followed by measuring the light resistance. The results
4 are shown in Table 19 below.

Table 19

Antioxidant	Optical Density (O.D.)		
	Irradiation time (0 hour)	Irradiation time (12 hours)	O.D. (12 hrs)/ O.D. (0 hr)
nil	0.85	0.38	0.45
hydroquinone	0.86	0.81	0.94
p-tert-butylcatechol	0.89	0.83	0.93
2,6-di-tert-butylphenol	0.90	0.83	0.92
methylhydroquinone	0.85	0.80	0.94
butylhydroxyanisole	0.84	0.79	0.94
diphenylamine	0.88	0.75	0.85
pyrogallol	0.83	0.79	0.95

19 Thus, the incorporation of the antioxidants in paper
20 is also effective in improving the light resistance.

21 Example 19

22 Example 11 was repeated using various UV absorbers,
23 with the results shown in Table 20 below, in which the
24

three recording papers are indicated as A'', B'' and C''
corresponding to recording papers A, B and C of Example 11.

Table 20 (1)

Rec- ording paper	UV absorber	Optical Density (O.D.)		
		Irra- diation time (0 hr)	Irra- diation time (12 hrs)	O.D. (12 hrs)/ O.D. (0 hr)
A''	nil	0.93	0.41	0.44
"	2-hydroxy-4- octoxybenzophenone	1.00	0.79	0.79
"	2-hydroxy-4- methoxybenzo- phenone	0.96	0.83	0.86
"	phenylsalicylate	0.91	0.70	0.77
"	p-t-butylphenyl salicylate	0.92	0.77	0.83
B''	nil	0.97	0.42	0.43
"	2-hydroxy-4- octoxybenzo- phenone	1.02	0.83	0.81
"	2-hydroxy-4- methoxy- benzophenone	0.98	0.82	0.84
"	phenyl salicylate	0.94	0.71	0.76
"	p-t-butylphenyl salicylate	0.93	0.74	0.80
C''	nil	0.88	0.35	0.40
"	2-hydroxy-4- octoxy- benzophenone	0.98	0.85	0.87

Table 20 (2)

Recording paper	UV absorber	Optical Density (O.D.)		
		Irra- diation time (0 hr)	Irra- diation time (12 hrs)	O.D. (12 hrs) / O.D. (0 hr)
C''	2-hydroxy-4-methoxy- benzophenone	0.91	0.76	0.84
"	phenyl salicylate	0.89	0.67	0.75
"	p-t-butylphenyl salicylate	0.90	0.69	0.77

These results show that the addition of the UV absorbers is effective in improving the light resistance.

Example 20

Various inks composed of 77 to 79 wt% of water, 20 wt% of ethylene glycol and 1 to 3 wt% of various dyes were made and applied on a recording paper D' which was made by incorporating 0.5 g/m² of 2-hydroxy-4-octoxybenzophenone as UV absorber in the coating layer of the recording paper A''. The light resistance was measured in the same manner as in Example 19. The results are shown in Table 21 below.

- 60 -

Table 21 (1)

Recording paper	Dye	Optical Density (O.D.)		
		Irradiation time (0 hr)	Irradiation time (12 hrs)	O.D.(12 hrs)/ O.D.(0 hr)
A''	C.I.Basic Violet 14	0.97	0.37	0.38
D''	"	0.99	0.81	0.82
A''	C.I.Basic Blue 3	0.79	0.46	0.58
D''	"	0.83	0.75	0.90
A''	C.I.Basic Yellow 11	0.57	0.39	0.69
D''	"	0.59	0.51	0.86
A''	C.I.Basic Red 1	0.79	0.35	0.44
D''	"	0.81	0.70	0.86
A''	C.I.Basic Red 13	0.78	0.56	0.72
D''	"	0.77	0.68	0.88
A''	C.I.Basic Yellow 17	0.51	0.21	0.41
D''	"	0.54	0.41	0.76
A''	C.I.Acid Orange 7	0.63	0.43	0.69
D''	"	0.63	0.58	0.92
A''	C.I.Acid Red 88	0.80	0.38	0.47
D''	"	0.77	0.69	0.90
A''	C.I.Acid Violet 49	0.92	0.32	0.35
D''	"	0.91	0.85	0.93

- 60 -

- 61 -

Table 21 (2)

Recording paper	Dye	Optical Density (O.D.)		
		Irradiation time (0 hr)	Irradiation time (12 hrs)	O.D.(12 hrs)/ O.D.(0 hr)
A''	C.I.Acid Blue 7	0.81	0.72	0.88
D''	"	0.85	0.78	0.92
A''	C.I.Acid Black 2	1.00	0.83	0.83
D''	"	1.05	1.04	0.99
A''	C.I.Acid Black 31	0.94	0.86	0.91
D''	"	0.95	0.91	0.96
A''	C.I.Direct Yellow 50	0.48	0.34	0.71
D''	"	0.49	0.43	0.88
A''	C.I.Direct Red 80	0.71	0.47	0.66
D''	"	0.70	0.60	0.86

The influence of the benzophenone on the light resistance more or less depends on the type of UV absorber but good results are obtained in all cases.

When the UV absorbers are applied by the surface coating technique, they are generally used in an amount of 0.1 to 10wt% of the coating composition of binder and

- 62 -

1 filler. Similarly to the antioxidants and compounds
2 capable of reacting with dye, larger amounts give an
3 adverse effect on the recording characteristics.

4 Example 21

5 A commercially available high quality paper showing a
6 relatively high degree of water absorptivity was used and
7 an ink jet recording using an ink of C.I. Basic Violet 10
8 was conducted on such paper. The recorded paper was then
9 dipped in an acetone solution of each of UV absorbers (2
10 wt%) and dried, after which it was subjected to the
11 measurement of light resistance. The results are shown in
12 Table 22 below.

14 Table 22

15	16 UV absorber	Optical Density (O.D.)		
		17 Irradiation time (0 hr)	Irradiation time (12 hrs)	O.D. (12 hrs)/ O.D. (0 hr)
18	nil	0.90	0.38	0.42
19	2-hydroxy-4-octoxy-	0.93	0.71	0.76
20	benzophenone			
21	2-hydroxy-4-methoxy-	0.91	0.77	0.85
22	benzophenone			
23	phenyl salicylate	0.89	0.68	0.76
24	p-t-butylphenyl salicylate	0.90	0.59	0.66

- 62 -

As will be clear from the above results, the dipping method is effective in improving the light resistance.

Exmple 22

LBKP having a freeness (C.S.F) of 400 ml was used as starting pulp to which were added 10wt% of talc, 2 wt% of a wet strength improver and 0.5 wt% of UV absorbers each based on the solid component of pulp. The thus added pulp were used to make papers with a basis weight of 50 g/m² in a usual manner.

Then an ink with the same composition as used in Example 21 was used and applied on the thusmade papers, followed by measuring the light resistance. The results are shown in Table below.

Table 22

UV absorber	Optical Density (O.D.)		
	Irradiation time (0 hr)	Irradiation time (12 hrs)	O.D. (12 hrs)/ O.D. (0 hr)
nil	0.82	0.39	0.47
2-hydroxy-4-octoxy-benzophenone	0.88	0.63	0.72
2-hydroxy-4-methoxy-benzophenone	0.85	0.67	0.79
phenyl salicylate	0.85	0.58	0.68
p-t-butylphenyl salicylate	0.81	0.51	0.63

- 64 -

1 The UV absorbers can be effectively utilized even by
2 the internal application method as will be apparently seen
3 from the above results.

- 64 -

Claims

1. An ink jet recording sheet which comprises a paper support applied on at least one surface thereof or internally with a composition characterized in that said composition comprises an aqueous dispersion of polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer or a mixture thereof serving as a binder or sizing agent and a white filler, said white filler being contained in a weight ratio to said binder of 10 : 1 to 0.2 : 1 when said composition is applied on the surface of said paper support and said composition comprises 10 to 60 parts by weight of said white filler and 2 to 20 parts by weight of said binder per 100 parts by weight of pulp when said composition is applied internally of the recording paper.
2. An ink jet recording sheet according to Claim 1, wherein said composition is applied on the surface of the paper support in an amount of 3 to 50 g/m² on a dry basis.
3. An ink jet recording sheet according to Claim 1, wherein said filler is clay, talc, calcium carbonate, calcium sulfate, calcium silicate, diatomaceous earth, magnesium silicate, terra alba, activated clay, magnesium oxide, magnesium carbonate or aluminium hydroxide in the form of a powder.

4. An ink jet recording sheet according to Claim 1, further comprising a binder resin used in combination with the first-mentioned binder resin, said first-mentioned binder resin being used in an amount of at least 20 wt% of the combination when the second-mentioned binder resin shows water absorptivity or in an amount of at least 33 wt% of the combination when said second-mentioned binder resin shows little water absorptivity.

5. An ink jet recording sheet according to Claim 1, further comprising a plasticizer to control a hardness of the film formed from the binder resin.

6. An ink jet recording sheet according to Claim 1, further comprising an aqueous emulsion-type resin or an alcohol-soluble resin, which shows a water proof property when dried in the form of a film, in an amount of 1 to 50 wt% of a combination with the binder resin, whereby the resulting coating is imparted with water proof.

7. An ink jet recording sheet according to Claim 1, further comprising 0.1 to 10 wt% of an antioxidant, UV absorber or compound capable of reacting with dye, so that the light resistance of an ink to be applied on the recording sheet is improved.

8. An ink jet recording sheet according to Claim 7, wherein the antioxidant, UV absorber or compound capable of reacting with dye is contained at least in the surface layer of the recording sheet.
9. An ink jet recording sheet according to Claim 7, wherein the antioxidant, UV absorber or compound capable of reacting with dye is contained in the recording sheet.
10. An ink jet recording sheet according to any of Claim 7 through 9, wherein the compound capable of reacting with dye is phosphorus tungstic acid, phosphorus molybdic acid or phosphorus tungsten molybdic acid.
11. An ink jet recording sheet according to claim 1, wherein the ratio is in the range of from 1 : 1 to 2 : 1.